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POLYNUCLEAR AROMATIC COMPOUNDS FOR HIGH TEMPERATURE LUBRICANTS

Best Available Copy

CHARLES F. RALEY, JR.
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NOVEMBER 1953

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POLYNUCLEAR AROMATIC COMPOUNDS FOR HIGH TEMPERATURE LUBRICANTS

Charles F. Raley, Jr.
Southwest Research Institute

November 1953

Materials Laboratory
Contract No. AF 33(616)-276
RDO No. 613-15

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

FOREWORD

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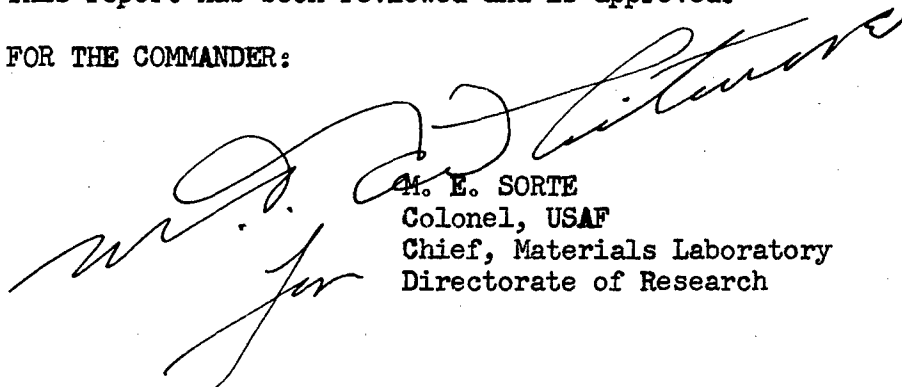
ABSTRACT

A literature survey covering the field of polynuclear aromatic compounds, with two or three nuclear rings, was made. All materials liquid at 35°C. and stable up to 400°F. were entered on file cards. From the data thus gathered, a list of seventeen compounds, considered to be representative of the common chemical structures, was compiled. These compounds were synthesized and evaluated as to thermal stability, viscosity at 100°F., 210°F., density, and boiling point. On the basis of this evaluation, the field of aryl phosphates was considered to have the most likely chance of providing compounds with the desired properties. Further research in this field has produced three liquid compounds with exceptional thermal stabilities, i.e., above 700°F.; di-p-tolyl 1-naphthyl phosphate, di-m-tolyl 1-naphthyl phosphate, and tri-o-chlorophenyl phosphate. In the case of the first two compounds, all other screening tests, such as flash and fire point, auto-genous ignition temperature and hydrolytic stability, gave ex-cellent results. Other compounds which will be synthesized offer a reasonable chance of possessing even better properties.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. E. SORTE
Colonel, USAF
Chief, Materials Laboratory
Directorate of Research

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I. INTRODUCTION

The severity of operating conditions of aircraft and related equipment has been steadily increasing. A resultant increase in operating temperatures has occurred, necessitating the development of lubricants and hydraulic fluids of much-improved thermal stability. Excessive sacrifice of low-temperature fluidity is undesirable, since storage and maintenance of equipment may be necessary in a very cold environment. One avenue of approach to the solution of this problem has been the investigation of chemical compounds of the polynuclear aromatic type.

Some of the factors indicating the desirability of research in this field are the high degree of oxidative stability of the aromatic ring, as well as the fact that the alkylated aromatics are among materials of known lubricating ability. In view of the oftentime high melting points of aromatics, the cold temperature requirement has been conservatively defined as fluidity at room temperature.

The plan of action, therefore, was to survey the literature to ascertain the present state of knowledge and then use this information as a guide to determine the most promising types of compounds to investigate.

This report contains the conclusions arrived at from the literature survey, the results of evaluating the survey compounds, and the results which have been obtained by research in the field of aryl inorganic esters.

II. DISCUSSION

A. Literature Search

The first phase of the work to be carried out on the project was a literature search to uncover all known low-molecular weight polynuclear aromatic compounds which would be stable up to

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205°C. (400°F.) and liquid at room temperature. In order to qualify as a low-molecular weight polynuclear aromatic compound, the compound had to meet the following requirements:

1) The compound shall have no less than two nor more than three fused rings in the nucleus. A ring attached to the nucleus by a spirane linkage is considered fused to the nucleus.

2) At least one fused ring in the nucleus shall be an intact benzene ring.

3) The non-benzene rings in the nucleus, if present, shall not be heterocyclic.

The compounds which met these specifications were then screened on the basis of melting point. A compound was defined as a liquid at room temperature if it had a melting point no higher than 35°C. (95°F.). In addition, the compound had to be stable up to 205°C. (400°F.).

The following information, if available, was recorded for each compound:

1. Boiling point

2. Melting point

3. Density

4. Molecular weight

5. Solubilities

6. Vapor pressure at 25°C. and 100°C.

7. Appearance

8. Thermal stability from 550°F. (288°C.) to 1000°F. (538°C.)

9. Viscosity in centistokes at 100°F., 210°F., and 400°F.

10. Cost

11. Availability

12. Method of preparation

13. Flash and fire point

14. Autogenous ignition temperature

15. Odor

16. Viscosity at constant rate of shear

17. Shear stability at various pressures

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The first course that was attempted was to cover
Chemical Abstracts in chronological order, beginning at 1907.
Entries were made not only for liquids but also for solids;
the cards on solids, however, were not further processed. The
subject entries shown in Table I were covered. This list was
compiled by searching "The Ring Index" (1) for the known ring
systems up to 1939 and individual Chemical Abstract Ring Indices
up to the present. The entries represent only the basic compound;
e.g., under naphthalene are also covered naphthoic acids, naphthols,
naphthylamines, naphthoquinones, etc.

The search was started August 1, 1952. The weakness of
the system of scanning Chemical Abstracts and recording both solid
and liquid compounds soon became apparent. One thousand references
were noted on cards within three days, and after six working days,
only a small percentage had been looked up. It became evident
that there was no possibility of completing the search within the
time limit of six weeks.

At this time, Volumes 12 and 13 of Elsevier's Encyclo-
pedia of Organic Chemistry became available, covering 2- and 3-
ring polynuclear aromatic compounds. It was therefore decided to
change the method of search in two respects: Elsevier would
constitute the main reference source, with gaps being filled in
from Beilstein and Chemical Abstracts; cards would not be made out
on solid compounds. The Chemical Abstracts for 1947, 1948, 1949,
and 1950 were searched using the 39 subject entries shown in Table
I. It is estimated that some 30,000 compounds were covered in all.

Using this plan, the search accelerated greatly. A bar
graph was made up showing the areas covered by the various reference
sources, facilitating the organization of effort. This graph is
shown in Figure 1. The search, covering the literature through 1950,
was completed September 8, 1952. It was not feasible to extend the
search past this date at the time, since the 1951 Subject Index of
Chemical Abstracts was not available; when the Index became avail-
able shortly thereafter, it was searched. In order to keep up with
current developments in the field, the individual issues of Chemical
Abstracts subsequent to 1951 are covered as they are received. In
order to cover compounds which are not published or available in
Chemical Abstracts, a search of the CBCC files and government tech-
nical reports was made.

The CBCC index of unpublished compounds, located at

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TABLE I. Subject Entries Covered In Chemical Abstracts

1. Acenaphthene
2. Acenaphthylene
3. Anthracene
4. Benzazulene
5. Benzindene
6. Benzocyclobutene
7. Benzycycloheptane (1907-1916)
8. Benzocyclooctatetraene
9. Benzonaphthene (Naphthindene)
10. Cyclobutadibenzene
11. Cyclodecabenzene
12. Cycloheptabenzene
13. Cycloheptanaphthalene
14. Cycloheptindene
15. Cyclooctabenzene
16. Cyclooctadibenzene
17. Cyclooctanaphthalene
18. Cyclopentindene
19. Cyclopropanaphthalene
20. Dibenzocycloheptadiene

21. Dibenzocycloheptatriene
22. Di-m-xylylene
23. 1,4-Ethanonaphthalene
24. Fluorene
25. Hydrindacene
26. Indacene
27. Indan
28. Indene
29. Isofluorene
30. Isoindene-2
31. 1,4-Methanonaphthalene
32. Naphthalene
33. Naphthindane (1907-1926)
34. Naphthindene (1907-1926)
35. Naphthazarin (1907-1926)
36. Phenanthrene
37. Spiro(cyclohexane-1,1^1-indan)
38. Spiro(cyclopentane-naphthalene)
39. Tetralin (before 1945)

4

1950
1949
1948
1947
1946
1944
1941
1936
1929
1907

Elsevier Vol. 12A — C.A. (1941)

Elsevier Vol. 12B-1 — C.A. (1944)

Elsevier Vol. 12B-2 — C.A. (1944)

Elsevier Vol. 12B-3 — C.A. (1944)

Elsevier Vol. 12B-4 — C.A. (1944)

Elsevier Vol. 12B-5 — C.A. (1944)

C.A. (1936)

Beilstein Vol. 9

Beilstein Vol. 14 — C.A. (1936)

Beilstein Vol. 10

Beilstein Vol. 11

Beilstein Vol. 14 — C.A. (1936)

Beilstein Vol. 16 — C.A. (1936)

Elsevier Vol. 13 — C.A. (1941)

C.A. 1946, 1947, 1948, 1949

Bicyclic compounds other than naphthalene

Naphthalene hydrocarbons and halogen compounds

Naphthalene nitrogen compounds

Naphthalene hydroxy compounds

Naphthalene keto compounds

Naphthalene quinones

Di-naphthyl, etc., methane

Naphthalene carboxylic acids

Naphthalene amino carboxylic acids

Naphthalene hydroxy and keto carboxylic acids

Naphthalene sulfonic acids

Naphthalene amino sulfonic acids

Naphthalene phosphines, organometallics, etc.

Tricyclic compounds

FIGURE I. Organization Of Literature Search

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1785 Massachusetts Avenue, Washington, D. C., was consulted August 25, 1952. The list of entries in Table I was coded for searching by an IBM machine. This search yielded some 2500 to 3000 reference cards. These cards were then screened by the melting point of the compound listed; the cards which had only a name and no properties were discarded. About fifty applicable compounds were found.

The OTS files in the T-5 building of the Department of Commerce were then scanned, using the following entries:

Aromatic compounds	Acid chlorides
Alcohols	Anthracene
Aldehydes	Naphthalene
Ketoaldehydes	Phenanthrene
Ketones	Indane
Amino compounds	Indene
Hydroxy aldehydes	Spirane
Aldols	Fluorene
Acids	Naphthols
Keto acids	Sulfur compounds
Oxy acids	Oxygen compounds
Hydroxy acids	Nitrogen compounds
Amines	Chlorine derivatives
Amides	Fluorine derivatives
Nitriles	Bromine derivatives
Diamines	Iodine derivatives
Polyamines	Lubricants

In this way, a list of reference numbers was obtained. These

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numbers were screened by referring to the Bibliography of PB reports, which covers PB, FIAT, CIOS, BIOS reports and those FD reports which were included in the PB reports. Then the OTS list of titles of AECD was consulted. The reference numbers which survived this screening were then referred to in the Library of Congress. No applicable compounds were found.

After the search itself was completed, it was necessary to classify the cards and to remove duplicates. Then the estimated normal atmospheric boiling point, obtained from the nomograph of Lippincott and Lyman (2), as well as a code denoting the atoms present, was entered on the cards for possible use in coding punched cards. The letters C, H, O, N, X, S, P, Si, and Q were used to designate their respective elements, Q being used to designate any other atom, and X representing halogen. A total of about 2400 compounds were incorporated in the card file. Since it was necessary to select a relatively small number of these which showed promising properties and appeared to be not too difficult to prepare for further investigation, it was decided to list:

1) All compounds having an observed boiling point of 260°C. (500°F.) or over, and

2) All compounds having a calculated normal boiling point of 372°C. (700°F.) or over.

In List 1 were 170 compounds; in List 2 were 499 compounds. Then to further narrow the field, the compounds duplicated on List 1 and List 2 were selected. In this way, a total of 39 compounds having observed boiling points of 260°C. (500°F.) or over and calculated normal boiling points of 372°C. (700°F.) or over remained. These compounds were individually examined for ease of preparation, yield, melting point, indicated stability to air and moisture, availability of starting materials, etc. A total of seven compounds survived this screening. These were termed Group I. These compounds, and those in Groups II and III, which are described below, are listed in Table II.

It is evident that the selection of compounds on the criteria mentioned depended considerably on subjective factors and therefore an element of uncertainty regarding the recommendations is bound to be present. However, this procedure was necessary in order to reduce the number of compounds under

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TABLE II. Selected Compounds From General File

Group I. Compounds With an Observed Boiling Point Above 260°C. (500°F.)
And a Calculated Normal Boiling Point Above 372°C. (700°F.).

Name Of Compound	Highest Lit. B.p., °C./mm. Hg.	Calc. Normal B.p., °C.	Melting Point, °C.	Bibliogra Referenc
Didodecylnaphthalene	282/5	490		592
x,x,x,-Tribenzylnaph-thalene	320-30/9	520		870
2-Hendecyl-naphthyl ketone	282/25	417		1561
1-and/or 2(α -Butyl-eicosanoyl)-naphtha-lene	280-300/4	492		1563
1-Naphthyl-(1-naphthyl-methyl)-acetonitrile	260-5/0.6	491		1849
Dicyclopentylace-naphthene	276-8/15	449		2183
Phenanthrene, phenyl-acetyl	262-4/0.6	540		2310

Group II. Compounds With an Observed Boiling Point Above 260°C. (500°F.) And a
Calculated Normal Boiling Point From 260°-372°C. (500°-700°F.).

Name Of Compound	Highest Lit. B.p., °C./mm. Hg.	Calc. Normal B.p., °C.	Melting Point, °C.	Bibliogra Referenc
2-Butylnaphthalene	282.5-83.5	282.5-83.5	-8	508
Butyltetralin	269-70	269-70	-62	510
2-tert-Butylnaphtha-lene	274-7/756	274-7	-4	524
tert-Butyltetralin	265-7	265-7	-49	525
1-Isoamylnaphthalene	303	303		534

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Name Of Compound	Highest Lit. B.p., °C./mm. Hg.	Calc. Normal B.p., °C.	Melting Point, °C.	Bibliography Reference
1-tert-Amylnaphthalene	301-3	301-3	--	536
1-Octylnaphthalene	335-7	335-7	-45	562
Octyltetralin	324-6/740	324-6	-51	565
1-Bromonaphthalene	281	281	6.2	933
1-Iodonaphthalene	305	305		935
4-Methyl-1-bromonaph-thalene	298	298	7	948
x-tert-Amyl-1-chloro-naphthalene	310-12	310-12		958
1-Dipropylamino-naph-thalene	above 300	above 300		1043
2-Dibutylamino-naph-thalene	355	355		1067
1-Butyloxy-naphthalene	308.5	308.5	2	1227
1-Isoamyloxy-naphtha-lene	317-19	318	below -10	1233
Isoamyl-1-naphthyl ketone	339-41/745	340		1553
Hexyl-1-naphthyl ketone	355-7/745	356		1554
Naphthalene-1-carboxy-lic acid, ethyl ester	309	309	6-8	1958
Naphthalene-2-carboxy-lic acid, isoamyl ester	265/100	346		1971

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Name Of Compound	Highest Lit. B.p., °C./mm. Hg.	Calc. Normal B.p., °C.	Melting Point, °C.	Bibliography Reference
1-Naphthyl orthosilicic acid, triethyl ester	308-20/744	341		2082
Phosphoric acid, 1-naphthyl ester dichloride	325-7	326		2090
1,2,3,4,5,6,7,8-Octahydrophenanthrene	295/760	295	16.7	2238

Group III. Compounds With A Calculated Normal Boiling Point Above 400°C. (750°F.)

Name Of Compound	Highest Lit. B.p., °C./mm. Hg.	Calc. Normal B.p., °C.	Melting Point, °C.	Bibliography Reference
2-(1-Indanyl)-2-cyclopentane malonic acid, diethyl ester	159/0.05	440		378
1-(β-Naphthyl)-2-methyl-cyclopentene	180-2/1	410		541
Dioctylnaphthalene	228-38/6	419		587
2-Octadecylnaphthalene	226-8/1	470		591
Trioctylnaphthalene	249-53/6	440		772
1-Methyl-x,x-dicyclopentylnaphthalene	192-9/1	420-30		807
1-m-Tolylnaphthalene	140-5/0.15	410		829
2-(4-Phenylbutyl)-5,6,7,8-tetrahydronaphthalene	236-7/13	400		857
2-o-Chlorobenzylnaphthalene	203-4/3	400		919
1-(1-Hydroxyheptyl)-naphthalene, ethyl ether	237-8/2-3	458		1177

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Name Of Compound	Highest Lit. B.p., °C./mm. Hg.	Calc. Normal B.p., °C.	Melting Point, °C.	Bibliography Reference
Diisopropyl-2-naph-thol	196/2	400		1178
1-(1-Naphthyl)-hep-tan-1-ol, n-decoate	224/2.5	440		1178.09
Dodecyl-1-naphthyl ether	210-1/3	411		1231
2-Nonyl-naphthyl ketone	246-7/8	413		1558
1-Dodecanoylnaphtha-lene	240-5/5	420		1559
1-Methoxy-4-caprylyl-naphthalene	258-60/14	410		1586
4-Phenyl-1-benzoylnaph-thalene	225-8/0.13	490		1629
6(or 7)-(4-Phenylbutyl)-1-keto-1,2,3,4-tetra-hydronaphthalene	214-16/0.01	560		1761
1-Naphthyl-(2-phenyl-ethyl)-acetonitrile	216-20/0.8	420		1847
Methyl-1-naphthyl-glyoxylate	200-40/5	400		1860
Benzyl-(1-naphthylmethyl)-malonic acid, diethyl ester	225-30/0.5	481		1940
Benzyl-(2-naphthylmethyl)-malonic acid, diethyl ester	225-30/0.3	500		1948
Naphthalene-1-carboxylic acid, d-2-undecyl ester	205/2.5	403		1966
Naphthalene-2-carboxylic acid, d-2-undecyl ester	206/2.5	405		1975
1,2,3,4-tetrahydrophen-anthrene, 9-bromo	142-5/0.05	450		2284

WADC TR 53-337

consideration drastically, and to insure that those selected could be produced in liter quantities in as short a time as possible.

The remaining compounds in List 1, namely those with an observed boiling point of 260°C. (500°F.) or over and a calculated normal boiling point of 260° to 372°C. (500° to 700°F.) were scanned in the same manner as previously mentioned. The compounds which remained, numbering 23, were called Group II.

In order to avoid overlooking compounds which have a high calculated normal boiling point but which have so far only low observed boiling points (under reduced pressure), a third group of compounds was compiled. This Group III consisted of compounds on List 2 which have calculated normal boiling points over 400°C. (750°F.). The total number of compounds in this group was 25.

. As a general observation, it may be seen that the alkylated and arylated aromatic nuclei constitute the largest class of compounds. Some 20 compounds, of the total of 55, fall in this class. It appears that hydrogenation of the nucleus lowers both the boiling point and the melting point, the latter more markedly. The alkylated tetralins and some alkylated naphthalenes exhibit remarkably low melting points. Esters are next in number, 11, with ketones closely following with 10. Halogen substituents on the nucleus are next most common (five each) with ethers (four each), nitriles and amines (two each) and naphthols concluding the list.

In the Quarterly Report No. 1 which covered the literature search, a complete tabulation of the compounds in the card file, with appropriate bibliography, was included. This tabulation is not reproduced in this report since the data is being transcribed to McBee punch cards which will constitute the entire reference source. This complete set of punch cards, together with a separate report covering the coding used thereon, will be forwarded to the Air Force upon completion of the project.

B. Synthesis Survey

Upon completion of the literature survey, a Steering Committee Meeting was held on October 7, 1952, at Wright-Patterson Air Force Base, to determine the course of future work.

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The compounds which have been presented in Table II were examined, and a group of fourteen were selected for synthesis. These compounds were considered to be representative of the major classes, which might be expected to exhibit the thermal stability necessary for high-temperature lubricants.

Subsequent to the choice of the fourteen compounds, the literature search, which was being continued, uncovered another compound that appeared very interesting due to its extremely high boiling point. This compound, diphenyl 2-naphthyl phosphate, together with its isomer, diphenyl 1-naphthyl phosphate, was included in the list of compounds to be synthesized. In the course of preparation of dicyclopentyl acenaphthene, the compound, cyclopentyl acenaphthene, was obtained as a by-product and was therefore added to the list, bringing the total to 17.

The plan of attack was to prepare these compounds and to subject them to the five screening tests listed below:

1) Physical state (visual)

2) Boiling point

3) Density

4) Viscosity at 100°F., 210°F., and 400°F.

5) Thermal stability

An attempt would then be made to relate the type and structure of the compound to its performance in the screening tests. In this way it was hoped to select particular classes of compounds which appeared to offer the most likely possibility of being suitable as high-temperature lubricants.

Upon completion of the synthesis survey, it was possible to come to a conclusion regarding the most promising approach. The data obtained in the program is presented in Table III.

Apparently, the substitution of cyclane groups on an aromatic nucleus results in a compound of poor thermal stability. It would appear that the tendency is to split off a cyclo-olefin. The ASTM slope of viscosities is about normal compared to the other alkylated aromatics listed. An examination of the monoalkyl naphthalenes shows that neither thermal stability nor ASTM slope is

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TABLE III. Physical Properties Of Selected Compounds

Class Of Compound	Name Of Compound	MLO Number	Viscosity, cs.			ASTM Slope 100°-210°F.	d_4^{25}
			100°F.	210°F.	400°F.		
Alkylated Aromatics	1-Octylnaphthalene	9502	10.72	2.09	0.59	1.000	0.9332
	2-Octyl-5,6,7,8-tetralin	9504	11.29	2.25	0.64	0.947	0.9092
	Trioctylnaphthalene	9503	79.69	7.18	1.22	0.838	0.9102
	Cyclopentylacenaphthene	9506	29.92	3.49	0.83	0.963	1.0694
	Dicyclopentylacenaphthene	9507	721.8	16.17	1.70	0.925	1.0622
	Tribenzylnaphthalene	9514	487	12.7	1.63	1.073	1.0986
Aryl Ethers	Butyl 1-naphthyl ether	9501	6.80	1.55	0.46	1.057	1.0180
	Isoamyl 1-naphthyl ether	9500	8.63	1.70	0.50	1.079	1.0040
Aryl Ketones	Isoamyl 1-naphthyl ketone	9510	12.10	2.19	0.64	1.009	1.0305
	Hexyl 1-naphthyl ketone	9511	12.97	2.11	0.68	0.942	1.0181
	Phenylacetyl phenanthrene	9512	--	36.88	1.88	1.104[b]	----
Halogenated Aromatics	1-Bromonaphthalene	9505	2.42	0.90	0.35	1.042	1.4847
Alkyl Carboxylates	2-Undecyl 1-naphthoate	9509	23.34	3.75	0.89	0.843	0.9873
	Diethyl benzyl-1-naphthyl-methylmalonate	9508	3147	26.6	1.69	0.933	1.1317
Inorganic Esters	Triethoxy-1-naphthyl-silane	9513	7.79	1.83	0.51	0.961	1.0560
	Diphenyl 1-naphthyl phosphate	9515	(120.0)[a]	7.02	1.26	0.944[b]	1.2468
	Diphenyl 2-naphthyl phosphate	9516	(100.0)[a]	6.56	1.23	0.941[b]	1.2395

a Extrapolated from the viscosities at 210°F. and 400°F.   b 210° - 400°F.

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TABLE III. Physical Properties Of Selected Compounds (Continued)

Class Of Compound	Name Of Compound	n_D^t Obsd.	B.p., °C. Obsd.	Thermal Decomp. Temp., °C. (°F.)	Calc. N.B.p. °C. (°F.)	M.p., °C.
Alkylated Aromatics	1-Octylnaphthalene	$1.5521^{23.5}$	107-111/0.13	>332(>629)	332(629)	-45
	2-Octyl-5,6,7,8-tetralin	$1.5138^{19.5}$	104-106/0.10	>322(>612)	322(612)	-51
	Trioctylnaphthalene	$1.5352^{23.5}$	170/0.21	352(666)	389(732)	
	Cyclopentylacenaphthene	$1.6123^{20.5}$	120-124/0.10	<210(<410)	359(678)	
	Dicyclopentylacenaphthene	$1.6190^{21.0}$	162-163/0.11	<240(<464)	452(846)	
	Tribenzylnaphthalene	$1.6492^{20.5}$	204/0.09	<302(<576)	510(950)	
Aryl Ethers	Butyl 1-naphthyl ether	$1.5795^{21.5}$	116/0.81	302(576)	307(584)	
	Isoamyl 1-naphthyl ether	1.5686^{25}	125-126/0.65	>306(>583)	306(583)	-10
Aryl Ketones	Isoamyl 1-naphthyl ketone	$1.5782^{25.5}$	111/0.10	>334(>633)	344(633)	
	Hexyl 1-naphthyl ketone	1.5719^{24}	122/0.08	>346(>655)	346(655)	
	Phenylacetyl phenanthrene	----	204/0.13	<310(<590)	480(896)	143
Halogenated Aromatics	1-Bromonaphthalene	$1.6574^{22.5}$	281/760	>281(>538)	281(538)	5-6
Alkyl Carboxylates	2-Undecyl 1-naphthoate	1.5351^{20}	161-164/0.14	<255(<491)	352(666)	
	Diethyl benzyl-1-naphthyl-methylmalonate	1.5760^{20}	172.5-175/0.065	<285(<545)	460(860)	54-56.5
Inorganic Esters	Triethoxy-1-naphthyl silane	1.5367^{21}	99-100/0.10	>307(>584)	307(584)	
	Diphenyl 1-naphthyl phosphate	----	201-207/0.12	>462(>864)	462(864)	53.5
	Diphenyl 2-naphthyl phosphate	----	203-210/0.14	>471(>880)	471(880)	64-65

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adversely affected by hydrogenating the unsubstituted ring. The mono-substituted naphthalenes appear to be more thermally stable in relation to their normal boiling points than the tri-substituted compounds. A comparison of trioctylnaphthalene with tribenzyl-naphthalene reveals the considerably better thermal stability of the trialkyl compound, as well as better viscosity characteristics.

The class of naphthyl alkyl ethers exhibits quite good thermal stability, which extends above their normal boiling points. The low viscosity values are coupled with a relatively high slope. The boiling points are relatively low, which is undesirable, although higher molecular weight homologs could quite possibly overcome this deficiency.

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The alkyl naphthyl ketones appear to have good absolute viscosity values and thermal properties although the A.S.T.M. slope is not very good. The remaining ketone, phenylacetyl phenanthrene, is really a supercooled liquid with poor properties in general.

The representative of the halogenated aromatics possessed quite good thermal stability, although it is a relatively low-boiling material. The viscosity slope is not good, and absolute viscosity values are much too low. This type of compound, in addition, is reported to be corrosive to metal surfaces.

The carboxylic esters exhibited quite poor thermal stability and, in the case of the highly-substituted malonic ester, poor viscosity characteristics. The viscosity characteristics of the simple ester, however, appear to be rather good. This poor thermal stability is probably due to disproportionation of the esters to free acid and olefin, and perhaps decarboxylation in the case of the malonate.

The last group, inorganic esters, proved to be the most promising, particularly in regard to thermal stability. The tri-ethoxy l-naphthyl silane was stable up to its rather low boiling point. This compound was apparently extremely susceptible to oxidation, since even one day's standing of the freshly distilled, pale-yellow liquid resulted in considerable darkening and the development of a bluish fluorescence. The isomeric diphenyl naphthyl phosphates were outstandingly thermally stable; they, however, possessed melting points higher than room temperature. The viscosity characteristics were not bad, since the A.S.T.M. slopes for these compounds are taken at 210°-400°F. and since these slopes are steeper than those taken at 100°-210°F.

It became quite apparent that by far the most promising class of compounds were the aryl esters of inorganic acids, specifically the phosphates. Of secondary interest would be alkylated aromatics and aryl ketones.

However, it was decided that the major effort would be devoted to exploring the field of phosphate esters, and such other inorganic esters as might appear to be of interest. It appeared quite feasible to retain most of the thermal stability of the aryl phosphates already synthesized, while improving the fluidity.

C. Research Based on the Synthesis Survey

The course of research which was followed in the final

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part of the year's work was the exploration of the field of aryl phosphate esters. It was thought that substitution of such groups as tetrahydronaphthyl and indanyl for naphthyl, and the use of tolyl, benzyl, pyridyl, etc., instead of phenyl, should lower the pour or melting point, with possibly not too much sacrifice of thermal stability.

The introduction of substituents on the aromatic ring often reduces the melting point of a compound containing that ring. For example, triphenyl phosphate has a melting point of 50°C., while tri-o-tolyl phosphate is a liquid.

Accordingly, the first modification of the diphenyl 1-naphthyl phosphate reference compound was replacement of the phenyl groups with m-tolyl. The results were quite promising. A tabulation of the properties of the phosphates which have been made thus far is found in Table IV.

A liquid state was achieved with a pour point of -15°C. (+5°F.). The thermal decomposition temperature was lowered to about 700°F., but it may be observed that it was still considerably better than any other compound previously made, except for the parent phosphates. It is also interesting to note that the viscosity slope was the best of all the compounds previously made, with the absolute viscosity values being quite good.

A preparation was then made of di-p-tolyl 1-naphthyl phosphate. Here again, the results were quite favorable. The viscosity slope was slightly poorer than that of the m-tolyl, as was the pour point (+10°F.), but the thermal decomposition temperature had increased to 740°F.

The properties of the two tolyl naphthyl phosphates were such that it was considered warranted to extend the testing procedure to the secondary tests outlined in the contract. In all these tests, both compounds exhibited excellent properties. These figures are given in Table V.

Since the introduction of a hetero-atom in an aromatic ring sometimes lowers the melting point, it was decided to prepare a compound having such a structure. Since quinoline melts considerably lower than naphthalene, -15°C. versus 80°C., it was decided to use this ring structure. Therefore, diphenyl 8-quinolyl phosphate was made.

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Table IV. Physical Properties of Selected Compounds

	Di-m-tolyl 1-naphthyl phosphate	Di-p-tolyl 1-naphthyl phosphate	Diphenyl 8-quinolyl phosphate
MLO Number	9518	9519	9520
Viscosity, cs.			
100°F.	104.6	126.9	225.8
210°F.	8.63	8.89	13.22
400°F.	1.42	1.39	1.68
ASTM slope (100-210°F.)	0.810[a]	0.850[b]	0.786
d_4^{25}	1.2946	1.2059	1.2801
n_d^t	$1.5967^{25.5}$	1.5955^{32}	$1.6040^{35.5}$
B.p., °C/mm	213-214/0.10	226-228/0.16	211-218/0.12
Calc. N.b.p., °C.(°F.)	447 (836)	473 (883)	449 (840)
Thermal Decomp. Temp. °C.(°F.)	373 (703)	394 (741)	330 (626)
M.p., °C.	-15[c]	-12[c]	58-59

a. 0.915 at 210-400°F.

b. 1.020 at 210-400°F.

c. pour point

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Table V. Secondary Tests on Promising Compounds

	Di-m-tolyl 1-naphthyl phosphate	Di-p-tolyl 1-naphthyl phosphate
MLO number	9518	9519
Flash point, °F.	575	530
Fire point, °F.	720	685
Solubilities, g./100 g.		
CCl_4	infinite	infinite
Benzene	infinite	infinite
Ethanol	infinite	infinite
Trichloroethylene	infinite	infinite
Water (cold)	insoluble	insoluble
Water (hot)	insoluble	insoluble
Skellysolve S	26.4	22.6
Hydrolytic stability mg. KOH/g. sample	0.00	0.05*
Autogenous ignition temp., °F.	>1400	>1400
Vapor pressure, mm.		
25°C.	1.4×10^{-8}	5.0×10^{-8}
100°C.	7.0×10^{-5}	1.2×10^{-4}
Mol. wt., obsd. (calc.)	409.7 (404)	410 (404)

* Within experimental error.

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The properties of diphenyl 8-quinolyl phosphate were inferior to the other phosphates made. The thermal decomposition temperature dropped considerably, to 616°F., and the melting point was higher than that of diphenyl 1-naphthyl phosphate. The compound appeared to darken on exposure to air, particularly at elevated temperatures. The viscosity slope, however, was relatively very good. This compound was not considered to justify further investigation.

Since chlorophenol might be considered a spatial isomer of cresol and has a low melting point, it was decided to make di-o-chlorophenyl 1-naphthyl phosphate. An additional consideration was that the halogen atom appears to be thermally stable, as was observed from data in the synthesis survey, in the case of bromonaphthalene. The methyl group of cresol apparently has some thermal instability, accounting for the lowered thermal-decomposition temperatures of the ditolyl 1-naphthyl phosphates. The attempt was made to prepare the intermediate di-o-chlorophenyl phosphoryl chloride from o-chlorophenol and phosphorus oxychloride, with anhydrous $MgCl_2$ catalyst, but the main product was tri-o-chlorophenyl phosphate, which appeared to be contaminated with di-o-chlorophenyl phosphoryl chloride. A thermal stability test gave the remarkable result of stability above 454°C. (850°F.) which was the normal boiling point. This is the highest thermal stability exhibited by any liquid compound prepared to date. Although chlorine-containing compounds have a reputation for metal corrosion and this particular compound is not polynuclear, it seems well worth-while to carry out the complete testing procedure on a purified sample. The preparation of di-o-chlorophenyl 1-naphthyl phosphate will also be carried out.

The preparation of dibenzyl 1-naphthyl phosphate, di-3-pyridyl 1-naphthyl phosphate and diphenyl 1-naphthyl thiophosphate has been attempted (several times in the case of the first two compounds) but the preparations thus far have been unsuccessful. Continuing attempts will be made to prepare these compounds, with the possible exception of the thiophosphate, in order to complete their preliminary evaluation.
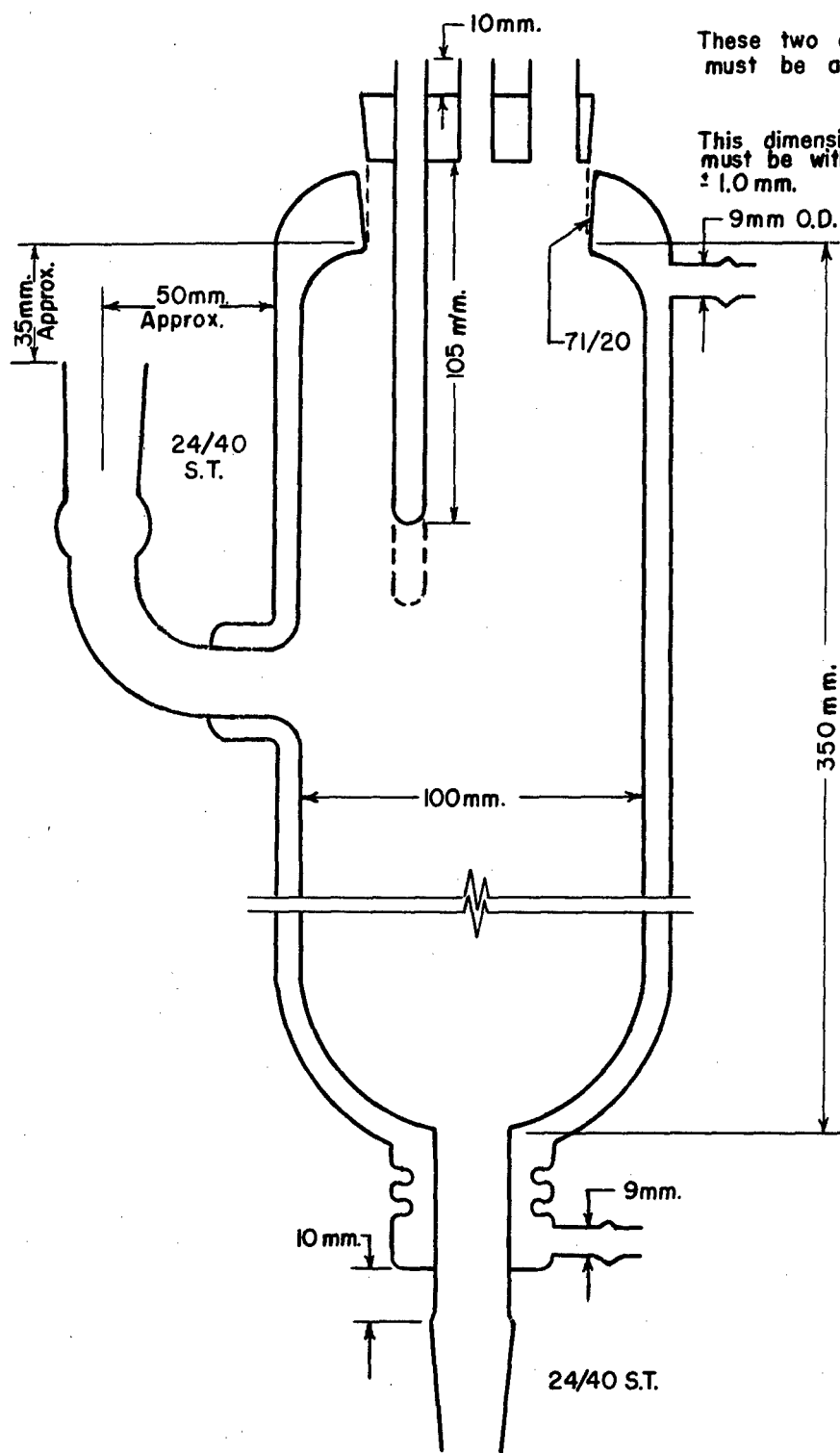
III. EXPERIMENTAL

A. Apparatus and Methods

    1. Thermal Stability. The method used for the determination

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of thermal stability involves the use of the isoteniscope to measure vapor pressure. In theory, the graph of log P (vapor pressure) versus the inverse of the absolute temperature is a straight line. When the compound starts to decompose, the vapor pressure increases non-uniformly, apparently due to the formation of volatile products, and departs from the straight line. This point of departure is the thermal decomposition temperature. The isoteniscope (3) is essentially a bulb attached to a U-tube manometer, and this to an air condenser. Both the method of determining thermal stability and the design of the isoteniscope were obtained from the Final Report of the University of Michigan on Wright Air Development Center Contract No. W-33-038-ac-21457, Project MX-982, dated December, 1952. By refluxing under vacuum the liquid being tested, the liquid accumulates in the U-tube, displacing the air present in the process. The isoteniscope is then cooled, and the liquid poured from the manometer back into the bulb, some liquid being allowed to remain to act as a liquid seal to exclude air. The process is repeated several times, to remove all traces of air. The temperature is then raised gradually, and the liquid legs in the manometer balanced by an applied external pressure. At a given temperature the applied pressure necessary to balance the manometer equals the vapor pressure. After considerable initial difficulty in eliminating sources of trouble in the apparatus, the method was found to be quite satisfactory, although tedious.
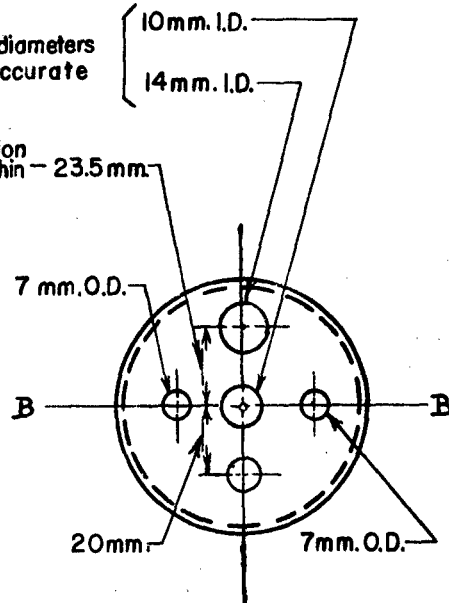
An air bath was tried at first for heating the isoteniscope, but was abandoned due to non-uniform temperature gradients. An aluminum block, heated by a flame, was found to give good results. The block is cylindrical, and surrounded by a glass shield; the block is provided with suitable recesses for inserting the isoteniscope and observing the manometer and bulb.

2. Viscosity at 400°F. In order to provide a 400°F. bath for viscosity determinations, consideration must be given to the problems inherent in maintaining such a relatively high temperature. If a liquid medium heated by some external source is used, the main difficulty is selecting a medium of sufficiently satisfactory oxidative and thermal stability. Continued transparency of the bath liquid is also necessary. Rather than use this method with its attendant complications, it was decided to use a refluxing liquid in an insulated chamber to provide the constant temperature. Accordingly, the apparatus depicted in Figure II was designed and built. The body of the apparatus is a double-walled chamber with provisions for evacuating the annulus, if desired. A side-opening accepts a condenser. The viscosimeter is inserted into the
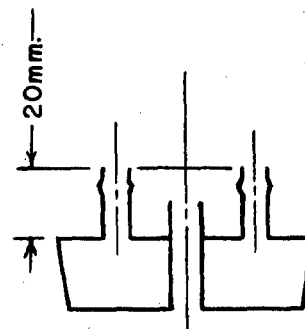
22

— 10mm.

These two diameters must be accurate

This dimension must be within ± 1.0 mm.

10mm. I.D. —
14mm. I.D. —

— 23.5mm.

— 9mm O.D.

7 mm. O.D. —

35mm. Approx.

50mm. Approx.

105 m/m.

—71/20

24/40 S.T.

B ——— B

20mm. —

7mm. O.D. —

TOP VIEW OF
STOPPER ASSEMBLY

350 mm.

100mm.

— 9mm.

10 mm.

24/40 S.T.

20mm.

SECTION B-B

Material — Pyrex glass
No. Req'd. — 1
Scale — 1/2

FIG. II

HIGH TEMPERATURE VISCOSIMETER BATH

WADC TR 53-337

central and large side holes in the plug and secured by rubber sleeves.
The plug is equipped with an inlet and outlet for passage of a cool-
ing medium to condense any vapor which might rise to the rubber sleeves.
An expansion bellows at the bottom of the jacket relieves strain
at high temperatures. It was found, at the barometric pressure pre-
vailing in San Antonio, that tetralin gave a vapor temperature of
400°F.

3. Molecular Weight. This property was determined by the cryo-
scopic method using benzene as a solvent.

4. Flash and Fire Point. The ASTM open cup procedure No. D
92-52 was used.

5. Solubilities. The solvent was added dropwise to a sample
of about 2 gm. of the material being tested. If the sample blended
with the solvent under the continuing dilution, the sample was rated
"infinitely soluble". If the sample did not blend with the solvent,
a second technique was used. This method was to add the sample drop-
wise from a microburette to a given volume of solvent and observe
the point where cloudiness occurs.

If as in the case of water the solubility of the sample were
less than 0.01 gm. of 150 cc. of solvent, the sample was termed
"insoluble".

6. Hydrolytic Stability. Ten grams of sample were added to
125 ml. of distilled water in a 500-ml. flask. The flask was agi-
tated for sixteen hours at 100°F. A 100 ml. sample of the water
layer, centrifuged if necessary for clarification, was titrated with
0.1 N KOH. The hydrolytic stability was reported as mg. KOH/gm.
sample.

7. Autogenous Ignition Temperature. A 125 ml. Erlenmeyer flask
was placed in a 4 in. porcelain evaporating dish containing about
one-half its volume of molten lead. A thermocouple was immersed
in the lead. The dish was heated with a gas-oxygen torch. The
temperature was gradually raised and at intervals a drop of sample
was dropped into the flask. The temperature at which the liquid
ignited was taken as the autogenous ignition temperature. A maxi-
mum workable temperature of about 1400°F can be attained by this
method. This is above the softening point of Pyrex glass.

8. Vapor Pressure at 25°C. and 100°C. These values were ob-
tained by extrapolation of the vapor pressure-temperature curves
obtained during the thermal stability test. An experimental spot

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check was made on di-m-tolyl 1-naphthyl phosphate at 100°C, using the transpiration method. Since the experimental value was 2.1 x 10^{-4} mm., compared with 0.7 x 10^{-4} obtained by extrapolation, and since the experimental error in measuring these low vapor pressures is quite high, the extrapolation was considered to give satisfactory results.

B. Chemical Syntheses

1. 1-Octylnaphthalene (MIO 9502) and Trioctylnaphthalene (MIO 9503).

Since the preparation of one of these compounds results in the formation of the other as a by-product, the two are described together. In the preparation of 1-octylnaphthalene, a 500 cc. three-neck, round-bottom flask equipped with reflux condenser, motor-driven stirrer and dropping funnel was charged with 128 gm. (1.0 mole) of naphthalene, 14.9 gm. of anhydrous $AlCl_3$ and 150 cc. of cyclohexane (as a solvent), and the flask was placed in an ice-bath. To the cyclohexane mixture was added dropwise with stirring 148.7 gm. (1.0 mole) of octyl chloride. After one hour, the addition was complete, and the reaction mixture was stirred for four more hours. The flask was then allowed to warm up to room temperature and left standing for fifteen hours. The reaction mixture was hydrolyzed with acidified water (5 vol.% conc. HCl and 95 vol.% H_2O), the organic layer separated off, washed twice with 500 cc. H_2O and dried over anhydrous $CaCl_2$. An emulsion which formed during the second washing was broken by the addition of NaCl.

After a preliminary topping at atmospheric pressure to remove volatile materials from the reaction product, the high-boiling residue was vacuum-fractionated. The resulting distillation curve (% distilled vs. b.p.) showed two distinct plateaus, belonging to mono-octyl and trioctylnaphthalene. These fractions were put aside until the trioctylnaphthalene preparation reached the same stage.

The trioctylnaphthalene preparation was carried out in an apparatus quite similar to that of the mono-octyl. The procedure varied somewhat. In the flask were placed 64 gm. (1/3 mole) of naphthalene, 223 gm. (1.0 mole) of octyl chloride and 75 cc. of cyclohexane as a solvent. The flask was cooled to -10°C and anhydrous $AlCl_3$ (22.3 gm.) added with stirring over a period of four hours. Then, after standing an additional four hours at 0°C, the reaction mixture was hydrolyzed with 500 cc. of dilute HCl (3.5%)

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and the organic layer separated off and washed with 500 cc. of 5% Na_2CO_3, 500 cc. H_2O and dried over anhydrous $CaCl_2$.

The reaction was topped at atmospheric pressure to remove volatile materials, as in the preparation of octylnaphthalene. Vacuum fractionation yielded a distillation curve having the same plateaus as previously obtained. In the first preparation, the mono-octyl plateau was somewhat the larger, while in the second, the trioctyl was considerably the larger.

The fractions from the mono-octyl plateaus of both runs were combined and refractionated, using a simple distilling head with a 6 cm. section packed with 3/16 in. helices. The product, b.p. 110°-116°/0.30 mm. $n_D^{23.5}$ 1.5521, weighed 74.4 gm. Based on the sum total of starting materials for both preparations, the yield was 20.6%.

The fractions from the trioctyl plateaus of both runs were also combined and refractionated using the same distilling head. The product, b.p. 170°/0.21 mm., $n_D^{23.5}$ 1.5352 weighed 69.0 gm. equivalent to a yield of 9.9%, based on the starting materials from both runs.

2. Butyl 1-Naphthyl Ether (MLO 9501) and Isoamyl 1-Naphthyl Ether (MLO 9500).

These two compounds are described together since their method of preparation is identical.

In a 500 cc., three-neck, round-bottom flask equipped with a reflux condenser and thermowell were placed 100 gm. (0.695 moles) of 1-naphthol, 231 gm. (3.12 moles) of n-butyl alcohol and 40 gm. of conc. H_2SO_4. The solution was refluxed at 113°C. for four hours, allowed to cool to 45°C, then poured into 500 cc. of water. After thorough shaking, the water layer was separated off; the organic layer was washed twice with 500 cc. of water and dried.

After topping the reaction mixture at atmospheric pressure, it was vacuum-distilled. The distillate contained considerable 1-naphthol. Most of this was removed by washing with 20% KOH, then with water. Two distillations of the alkali-washed material gave 59.8 gm. of product, b.p. 116°/0.81 mm., $n_D^{21.5}$ 1.5795. The yield was 43.0% of the theoretical.

The preparation of isoamyl 1-naphthyl ether was carried out in

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the same manner. The reaction mixture consisted of 100 gm. (0.695 moles) of 1-naphthol, 275 gm. (3.12 moles) of isoamyl alcohol and 40 gm. of conc. H_2SO_4. Refluxing for four hours at 122°C. was carried out, followed by washing of the reaction product once with 400 cc. H_2O, then with 200 cc. H_2O, twice with 200 cc. portions of 20% KOH, and once with 3% HCl solution. After drying, the reaction mixture was topped up to 195°C. at atmospheric pressure. After repeated distillation, with removal of solid 1-naphthol, 67.8 gm. of isoamyl 1-naphthyl ether, a refractive colorless liquid, b.p. 125°-126°/0.65 mm., $n_D^{21.5}$ 1.5707 was obtained. The yield was 45.5% of theory.

3. **Cyclopentylacenaphthene (MLO 9506) and Dicyclopentylacenaphthene (MLO 9507).**

In a 500 cc., three-neck, round-bottom flask equipped with a mechanical stirrer, reflux condenser closed with a $CaCl_2$ drying tube, and a dropping funnel, were placed 104 gm. (0.675 moles) of acenaphthene, 20 gm. of $AlCl_3$ and 250 cc. of cyclohexane as a solvent. The flask was placed in an ice-bath and 200 gm. (1.35 moles) of cyclopentyl bromide was added dropwise. After addition was complete, the reaction mixture was stirred for 3.5 hours, then allowed to come to room temperature during three more hours. After hydrolysis with dilute HCl, and washing three times with water, the product was dried over anhydrous $MgSO_4$.

After topping of the reaction mixture to remove volatile material, the usual series of vacuum distillations were carried out. It was apparent that two fractions were present. In the course of these distillations, it appeared that the heavier fraction was breaking down to the lighter. In this way was obtained cyclopentylacenaphthene (the lower-boiling fraction), a yellow liquid, b.p. 118°-128°/0.11 mm., $n_D^{20.5}$ 1.6123; molecular weight (calc.) 222, (obsd.) 223. The yield was 25.9%.

The higher-boiling fraction, dicyclopentylacenaphthene, was a very viscous, refractive yellow liquid, b.p. 162°-163°/0.11 mm., n_D^{21} 1.6190; molecular weight (calc.) 290, (obsd.) 288. The yield was 10.8%.

4. **2-Octyl-5,6,7,8-Tetralin (MLO 9504).**

Following the procedure used in the above-described Friedel-Crafts syntheses, a 500 cc., three-neck, round-bottom flask was equipped with a mechanical stirrer, dropping funnel and condenser

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with drying tube. The flask was placed in an ice-bath and charged with 132 gm. (1 mole) of tetralin (redistilled, b.p. 206°-207°), 21 gm. of $AlCl_3$, and 150 cc. of cyclohexane. The octyl bromide was added dropwise with stirring, over a period of four hours. The reaction mixture was allowed to stand fifteen hours, hydrolyzed by dilute HCl and washed twice with water, then dried over anhydrous $CaCl_2$.

The reaction mixture was distilled at atmospheric pressure to remove solvent and unreacted starting materials. The residue, after two vacuum fractionations, gave 48.5 gm. of octyltetralin, b.p. 112°-120°/0.31 mm., $n_D^{19.5}$ 1.5138 (literature n_D^{20} 1.5138); molecular weight (calc.) 244, (obsd.) 246. The yield was 20.0%.

5. **Isoamyl 1-Naphthyl Ketone (MIO 9510) and Hexyl 1-Naphthyl Ketone (MIO 9511).**

A 1-mole quantity of isoamylmagnesium bromide in ether was prepared in the customary way, then reacted with a solution of 136.5 gm. (0.89 moles) of 1-naphthonitrile in 300 cc. of anhydrous toluene. After one hour the addition of the toluene solution was complete. An additional 300 cc. of toluene was added and the ether in the reaction mixture distilled off. Another 300 cc. portion of toluene was required near the end of the ether removal. The ether-free toluene solution was then refluxed for one hour.

The reaction mixture was hydrolyzed with 500 cc. of ice-cold saturated NH_4Cl. Vigorous stirring was continued for about 1/2 hour. A persistent emulsion formed which was broken by cut and try use of solvents and NaCl. The aqueous layer was washed once with 250 cc. of ether and the ether layer combined with the original organic layer.

The organic layer was twice extracted with 500-cc. portions of 9N. H_2SO_4. The acid layers were combined and extracted once with 250 cc. of ether. The aqueous layer containing the ketimine sulfate was refluxed for two hours, then allowed to cool.

This aqueous layer was washed twice with 400-cc. portions of an equivolume mixture of ether and benzene. The ether-benzene layers were combined and washed once with 400 cc. of H_2O, twice with 400-cc. portions of saturated Na_2CO_3 and twice with 400-cc. portions of saturated NaCl. The ether-benzene solution was then dried over anhydrous $MgSO_4$.

After removal of the solvent by atmospheric distillation,

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subsequent vacuum distillations yielded 44.1 gm. (21.8% of the theoretical) of isoamyl 1-naphthyl ketone, a yellow, refractive oil, b.p. 111°/0.10 mm., $n_D^{25.5}$ 1.5782, d_4^{25} 1.0305.

The hexyl 1-naphthyl ketone was made in an entirely similar way. To a solution of Grignard reagent, made from 24 gm. (1 mole) of Mg and 165.1 gm. (1 mole) of hexyl bromide in anhydrous ether, was added dropwise a solution of 145 gm. (0.95 moles) of 1-naphthonitrile in 300 cc. of anhydrous toluene. Carrying through the preparation as described above gave 18.9 gm. (7.9% of theory) of hexyl 1-naphthyl ketone, a yellow, refractive oil, b.p. 122°/0.08 mm., n_D^{24} 1.5719, d_4^{25} 1.0181.

6. Tribenzylnaphthalene (MIO 9514)

Three attempts were made to prepare this material; in each case only very small amounts of product, of dubious purity, were obtained. The product in all cases appeared to be a narrow-cut fraction of a mixture of substances.

Run 1. In a 1-liter, three-neck, round bottom flask equipped with reflux condenser protected by a $CaCl_2$ tube, mechanical stirrer and gas inlet tube were placed 192 gm. (1.5 moles) of naphthalene and 486 gm. (4.5 moles) of benzyl alcohol. Into the flask, through a safety trap, was bubbled gaseous BF_3, supplied by a cylinder. After one hour, the mixture cleared and took on a bluish fluorescence. Considerable heat was liberated, and a cold water bath was used to remove some of the heat. On continued passage of BF_3, two layers separated. The viscous reaction mixture was poured into H_2O and the organic material taken up in 500 cc. of ether. The ether layer was washed twice with 500 cc. of 5% KOH and twice with 500 cc. of H_2O. After drying the ether layer over anhydrous $MgSO_4$, the ether was distilled off. Vacuum distillation of the viscous residue gave a fraction, a cloudy, pale-yellow, viscous liquid, b.p. 204°/0.09 mm., $n_D^{20.5}$ 1.6492, d_4^{25} 1.0986. The weight was 21.3 gm. or 3.6% of the theoretical. The distillation residue was a glass and was preponderantly the major fraction.

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Run 2. This run was carried out in the same manner as Run 1. However, since alkylation appeared to go beyond the tri-substituted compound in Run 1, a 1:1 mole ratio of benzyl alcohol to naphthalene was used. The reagents used were 384 gm. (3 moles) of naphthalene and 324 gm. (3 moles) of benzyl alcohol. Working up the reaction product gave 17.0 gm. of a cloudy viscous liquid, b.p. 217°-228°/0.09 mm., n_D^{25} 1.65534. The yield was 4.3%. A major amount of benzylnaphthalene apparently was formed.

Run 3. In a 1-liter, three-neck, round-bottom flask fitted with a mechanical stirrer and reflux condenser were placed 128 gm. (1 mole) of naphthalene, 379.8 gm. (3 moles) of benzyl chloride, and 280 cc. of CS_2. Addition of 38 gm. (10 wt.% based on halide used) of $AlCl_3$ was started but after about 2 gm. had been added, a sustained reaction occurred and some of the reaction mixture foamed out of the flask. No significant temperature rise was noted, but evolution of HCl was copious. A considerable amount of the CS_2 was boiled off. The reaction mixture became purple, then black. When the initial reaction had subsided, ice-cooling having been employed, the rest of the $AlCl_3$ was added in small portions without incident. After addition was complete, the mixture was stirred for one hour and hydrolyzed in 3% HCl. The lower, organic, layer was separated off, and the water layer washed once with ether. The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of solvent, two vacuum distillations gave 13.6 gm. (3.4% yield) of a cloudy, viscous, orange oil, b.p. 210°-220°/0.10 mm., n_D^{23} 1.6541.

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7. Phenylacetyl Phenanthrene (MLO 9512).

In a 1-liter, 3-neck round-bottom flask fitted with a mechanical stirrer and reflux condenser closed with a CaCl2 tube were placed 178.2 gm. (1 mole) of phenanthrene, 154.6 gm. (1 mole) of phenylacetyl chloride and 400 cc. of CS2. The flask was cooled in an ice-bath and 160.0 gm. (1.2 moles) of AlCl3 was added in small portions with stirring. The reaction mixture turned black. After all the AlCl3 had been added, the reaction mixture was stirred for fifteen hours, then hydrolyzed in 1 liter of 3% HCl. The lower, organic, layer was separated off, and the aqueous layer washed with 400 cc. of ether. The ether and CS2 layers were combined, diluted with 400 cc. of ether, then washed with 300 cc. of saturated NaCl solution. The organic layer was separated off and dried over anhydrous MgSO4. After removal of the solvent, the residue was vacuum distilled. The yield was 162.9 gm. (55% of the theoretical) of phenylacetyl phenanthrene, b.p. 204°/0.13. The distillate was an orange glass which slowly deposited crystals, especially on moderate warming. The crystals melted at 142.2°-143.4°C.(corr.); the literature (4) melting point is given as 140°C.

8. 2-Undecyl 1-Naphthoate (MLO 9509).

a. 2-Undecyl alcohol

A 1-mole preparation of methylmagnesium iodide was carried out in anhydrous ether in the usual manner. To the solution of Grignard reagent was added with stirring 156 gm. (1 mole) of decyl aldehyde dissolved in 200 cc. of anhydrous ether. The addition was dropwise over a period of 2 1/2 hours. The reaction product was then hydrolyzed by the addition of 100 cc. of H_2O added dropwise followed by 100 cc. of conc. HCl diluted with 100 cc. of H_2O. Two clear layers resulted.

The ether layer was washed with 500 cc. of H_2O, then twice with 500 cc. portions of 5% KOH. After two more washings with 500 cc. of H_2O, the ether layer was dried over anhydrous MgSO4. After removal of the ether, the residue was distilled at atmospheric pressure, giving 94.5 gm. of 2-undecyl alcohol, a water-white oily liquid, b.p. 219°-220°, n_D^{21} 1.4378 (Beil. I, 427; n_D^{21} 1.4369). The yield was 54.8%.

To 94.5 gm. (0.548 moles) of 2-undecyl alcohol were added 94.5 gm. (0.548 moles) of 1-naphthoic acid. To the acid-alcohol mixture was added 3 cc. of conc. H_2SO_4 and 200 cc. of dry benzene.

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The reaction vessel was fitted with a water separator, and the reaction mixture refluxed until the volume of water taken off appeared not to increase. The refluxing time was about 72 hours.

After refluxing was stopped, the liquid in the flask was black. On cooling a soft crystalline mass formed. To the mixture was added 200 cc. of ether, the solution filtered, and the ether solution washed with 200 cc. of H_2O, then twice with 250 cc. of 5% KOH, then twice with water. The final water wash produced an emulsion which was broken by the addition of solid NaCl. After drying the ether solution over anhydrous $MgSO_4$ and distilling off the ether, the residue was vacuum distilled. The 2-undecyl 1-naphthoate was obtained as a yellow, refractive liquid, b.p. 161°-164°/0.14 mm., n_D^{20} 1.5351. The weight was 59.3 gm., equivalent to a yield based on the esterification step only, of 33.0%.

9. Diethyl Benzyl-1-naphthylmethylmalonate (MLO 9508).

   a. Diethyl benzylmalonate (5)

   In a 1-liter, 3-neck, round-bottom flask equipped with a reflux condenser, mechanical stirrer and dropping funnel was placed approximately 500 cc. of absolute ethanol. The alcohol was stirred and gradually 23 gm. (1 mole) of clean Na were added through the condenser. Too violent reaction requires cooling of the flask. The solution was allowed to cool to 50° C., then 165 gm. (1.03 moles) of diethyl malonate was added through the dropping funnel. If the flask is allowed to cool below about 50° C. the addition compound precipitates.

   To the clear solution of diethyl sodiomalonate was added gradually with stirring 126.5 gm. (1 mole) of benzyl chloride. After addition is complete, the reaction mixture is refluxed for two hours, at the end of which time it was neutral to litmus.

   Upon adding 400 cc. of H_2O and warming, the pasty residue dissolved. The mixture was shaken thoroughly and the water separated off. Vacuum distillation yielded a water-white fraction, b.p. 136°-152°/2.3 mm., n_D^{21} 1.4870, weighing 120.3 gm. This, calculated as diethyl benzylmalonate (b.p. 137°-138°/3 mm.), is equivalent to a 48% yield.

   A solution of sodium ethoxide was again made in the same manner from 11.1 gm. (0.48 moles) of Na and 350 cc. of absolute ethanol. To the solution of sodium ethoxide was added slowly 120.3 gm. (0.48 moles) of diethyl benzylmalonate. The reaction mixture was

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allowed to stand for fifteen hours. To the reaction product was added dropwise with stirring 85.0 gm. (0.48 moles) of 1-chloromethyl naphthalene. After addition was complete, the reaction mixture was refluxed for three hours and then most of the alcohol removed by distillation. When foaming became excessive, the distillation was stopped.

After diluting the product with 400 cc. of ether, and washing the ether solution with 400 cc. of H_2O, the ether solution was dried over anhydrous $MgSO_4$. After removal of the ether, and vacuum distillation, the product, diethyl benzyl-1-naphthylmethylmalonate, was recovered as a very viscous, pale-yellow oil, b.p. 172.5°-175°/0.065 mm., n_D^{20} 1.5760. The weight of the product was 128.6 gm. which corresponds to a yield of 68.5%. The observed molecular weight in benzene was 386; calculated, 390.

It was found that the product crystallized on standing to a solid, m.p. 54°-56.5° C.

10.   Triethoxy 1-Naphthylsilane (MLO 9513).

In a 2-liter, 3-neck, round-bottom flask equipped with a reflux condenser, mercury-sealed stirrer and dropping funnel, and with the system protected from moisture by a Gilman bridge, was prepared a 1-mole quantity of 1-naphthylmagnesium bromide, following the usual Grignard technique. To the solution of Grignard reagent was added with stirring 208.3 gm. (1 mole) of tetraethyl orthosilicate. After initial thickening of the reaction mixture, it became quite fluid when addition was complete. Stirring was continued for two hours and the reaction mixture allowed to stand for sixty hours.

A yellowish solid had settled out. The mixture was filtered and the ether distilled off. Vacuum distillation yielded 34.7 gm. of a brownish-yellow oil, b.p. 99°-100°/0.10 mm., n_D^{21} 1.5367. The yield was 12%. The product darkened rapidly and acquired a strong blue fluorescence on standing.

11.   Diphenyl 1-Naphthyl Phosphate (MLO 9515) And Diphenyl
        2-Naphthyl Phosphate (MLO 9516).

a.   The first step in the preparation of the above compounds, which are made in the same way, is the synthesis of diphenyl phosphoryl chloride. A typical preparation is described. In a 2-l. flask equipped with a reflux condenser and thermowell were placed 612 gm. (4 moles) of $POCl_3$ and 752 gm. (8 moles) of phenol. The

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temperature was brought to 200°C. as rapidly as possible and was held there for four hours. (Using a 2-l. Glas-Col heating mantle, 70 v. was applied, then reduced to 45 v. when 200°C. was reached.) After two distillations, the diphenyl phosphoryl chloride was obtained. This was a water-white, refractive liquid, b.p. 172°/5 mm. The weight was 533.6 gm. or 49.5% of theory.

b. To a solution of 134 gm. (0.5 moles) of diphenyl phosphoryl chloride in one pound of pyridine was added 72 gm. (0.5 moles) of 1-naphthol. After standing for about sixty hours, the reaction mixture was diluted with five pounds (1425 cc.) of CCl$_4$ and washed four times with one-liter portions of water. The organic layer was dried over anhydrous MgSO$_4$. After distillation up to 150°C. (flask temperature) at atmospheric pressure to remove volatile solvent, the reaction product was heated to 155°/40 mm. (water aspirator) to complete the removal. Two vacuum distillations then gave 106.2 gm. of diphenyl 1-naphthyl phosphate, a viscous, refractive orange liquid which crystallized on standing, b.p. 201°-207°/0.12 mm. The yield was 56.5% of theory. Upon three recrystallizations from 95% ethanol, the melting point was 53.5°C. The recrystallized solid was creamy white.

c. To prepare diphenyl 2-naphthyl phosphate, 130 gm. (0.55 moles) of diphenyl phosphoryl chloride was dissolved in one pound of pyridine and 79.2 gm. (0.55 mole) of 2-naphthol added. Some heat of reaction was observed. The flask was cooled to room temperature and allowed to stand seventeen hours. To the reaction mixture was added five pounds of CCl$_4$, as before, and the solution washed four times with one-liter portions of water. After drying the organic layer over anhydrous MgSO$_4$, the volatile components were distilled twice. The product, diphenyl 2-naphthyl phosphate, b.p. 203°-210°/0.14 mm. was a viscous, refractive orange liquid which crystallized on standing. Three recrystallizations from 95% ethanol gave a creamy white product melting at 64°-65°C. The yield of distillate was 66.8 gm. or 32% of the theoretical.

12. Di-m-Tolyl 1-Naphthyl Phosphate (MLO 9518) And Di-p-Tolyl 1-Naphthyl Phosphate (MLO 9519)

    a. Di-m-Tolyl 1-Naphthyl Phosphate

       (1.) Di-m-tolyl phosphoryl chloride

       In a 1-liter flask, fitted with a thermowell and an 80 cm. water-cooled reflux condenser, were placed 244.8 gm. (1.6 moles)

of $POCl_3$ and 346.0 gm. (3.2 moles) of m-cresol. The reaction mix-
ture was brought as rapidly as possible to 200°C. (Using a 1-liter
Glas-Col heating mantle, it was found advantageous to apply 70 volts
until the temperature reached 200°C, then reduce the voltage to 45 v.)
The mixture was kept at 200° for three hours, and the solution then
allowed to cool. Two vacuum distillations gave 203.5 gm. of di-m-tolyl
phosphoryl chloride, a water-white oily liquid with a faintly pungent
odor, b.p. 184°/5.5 mm., n_D^{24} 1.5440. The yield was 43%.

(2.) Di-m-tolyl 1-naphthyl phosphate

To a solution of 86.4 gm. (0.6 moles) of 1-naphthol
dissolved in 460 cc. of pyridine was added 178.0 gm. (0.6 moles) of
di-m-tolyl phosphoryl chloride.

After standing for fifteen hours, the reaction mixture
was diluted with 5 lb of CCl_4, washed four times with 1-liter portions
of water, then dried over anhydrous $MgSO_4$. After removal of solvent
and purification of the residue by vacuum distillation, the product
was obtained as a fairly viscous, orange-yellow, refractive oil, b.p.
213°-214°/0.10 mm., $n_D^{25.5}$ 1.5967. The weight of di-m-tolyl 1-naphthyl
phosphate was 129.0 gm. equivalent to a 53.3% yield.

b. Di-p-tolyl 1-Naphthyl Phosphate

(1.) Di-p-tolyl phosphoryl chloride.

In a 1-liter flask equipped with a thermowell and an
80 cm. straight-bore water condenser were placed 245 gm. (1.6 moles)
of $POCl_3$ and 346 gm. (3.2 moles) of p-cresol. The reaction mixture
was brought as rapidly as possible to 200°C, using the same voltages
on the heating mantle as described in the preceding preparation, and
was held there for four hours. The reaction product was vacuum dis-
tilled twice to give 293 gm. of di-p-tolyl phosphoryl chloride, a
water-white, refractive, somewhat viscous liquid with a moderately
pungent odor, b.p. 192°/5 mm., n_D^{19} 1.5456, d_4^{25} 1.2946.

(2.) Di-p-tolyl 1-naphthyl phosphate.

To a 1-liter flask containing one pound of pyridine
was added 142 gm. (0.988 moles) of 1-naphthol. To the naphthol
solution was added 293 gm. (0.988 moles) of di-p-tolyl phosphoryl
chloride. After standing for fifteen hours, the reaction mixture
was diluted with five pounds of CCl_4 and the solution was washed in

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turn with one liter of water, one liter of 5% KOH, one liter of water, one liter of 3% HCl, and one liter of water. After drying the organic layer over anhydrous $MgSO_4$, the volatile components were removed by atmospheric distillation up to 165°C. (flask temperature) followed by stripping up to 200°C/32 mm. Three vacuum distillations of the residue gave 261.5 gm. of di-p-tolyl 1-naphthyl phosphate, a yield of 65.5%. The product was a faintly yellow, moderately viscous liquid, turning greenish on standing. The boiling point was 226°-228°/0.16 mm., n_D^{32} 1.5955, d_4^{25} 1.2059.

13. Diphenyl 8-Quinolyl Phosphate (MLO 9520).

To a solution of 145 gm. (1 mole) of 8-hydroxyquinoline in one pound of pyridine was added 268.5 gm. (1 mole) of diphenyl phosphoryl chloride, the preparation of which has already been described. Some heat was liberated, so the temperature was reduced by cooling the reaction vessel with tap water. After standing for about thirty-six hours, crystals had formed. The reaction mixture was diluted with five pounds of CCl_4, then washed in turn with one-liter quantities of water, 5% KOH, water, 3% HCl, and water. After drying the solution over anhydrous $MgSO_4$, the volatile materials were removed by distillation up to a flask temperature of 154°C at atmospheric pressure, then up to 199°C at 32 mm. Four vacuum distillations gave 209 gm. of diphenyl 8-quinolyl phosphate, b.p. 211°-218°/0.12 mm., $n_D^{35.5}$ 1.6040, d_4^{25} 1.2801, equivalent to a yield of 58.0%. The product was a lemon-yellow oil which crystallized on standing to a solid melting at 58-59°C. Exposure to air appeared to cause slow darkening.

14. Tri-o-Chlorophenyl Phosphate (MLO 9522).

In an attempt to prepare di-o-chlorophenyl phosphoryl chloride, 386 gm. (3.0 moles) of chlorophenol was added to 230 gm. (1.5 moles) of $POCl_3$ in a 1-liter flask equipped with a water condenser and thermowell. Then 15.4 gm. of anhydrous $MgCl_2$ was added as a catalyst and the mixture was heated to 200°C. After one hour, the reaction mixture was allowed to cool. [The anhydrous $MgCl_2$, proposed as a catalyst by Caprio and Shuman (6), was prepared by heating 43.6 gm. of $MgCl_2 \cdot 6H_2O$ in a procelain crucible until the initial melt had completely re-solidified. The anhydrous salt was immediately ground and added to the reaction mixture.] Upon distillation no plateau corresponding to the expected boiling point of about 165°-175°/0.1 mm. was found (8). The major product was 150 gm. of a fraction boiling at 188°-189°/0.11 mm., n_D^{34} 1.5791, d_4^{25} 1.4126. The molecular weight was determined to be 423.5; the molecular weight calculated for tri-o-chlorophenyl phosphate was 429.5. There seemed to be, however, a

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certain amount of acid chloride present, since a pungent odor became apparent on standing and because addition of an alcohol in pyridine liberated considerable heat.

Therefore, to 127.7 gm. (0.3 mole) of the apparently impure tri-o-chlorophenyl phosphate was added a large excess 62.6 gm. (0.49 mole), of o-chlorophenol, and 200 cc. of pyridine. A fairly large amount of heat was evolved. After standing for about fifteen hours, the reaction mixture was diluted with 500 cc. of CCl_4, then washed in turn with 500 cc. portions of water, 5% KOH, water, 3% HCl and water. The solution was dried and the solvent stripped off. The residue was vacuum distilled three times to give 85.7 gm. of water-white, fairly viscous liquid, b.p. 203°/0.19 mm., $n_D^{30.5}$ 1.5811. The liquid had a faint odor resembling o-chlorophenol.

15. Thiotenol (5-Methyl-2-Hydroxythiophene).

The procedure of Paal (7), modified somewhat, was used. A 1-liter 3-neck, ground joint flask was fitted with a thermowell, distilling head and slurry reservoir. The slurry reservoir consisted of a 500 cc. flask with a tubulature at the bottom, mounted above one of the side arms of the reaction flask. This side arm was fitted with a dropping tip. The tubulature of the slurry reservoir was connected by a short section of rubber tubing to the dropping tip in the side arm. The slurry reservoir was equipped with a mechanical stirrer. A pinch clamp was placed on the rubber tubing connector. In the slurry reservoir was placed 348 gm. (3.0 moles) of levulinic acid and 222 gm. (1.0 mole) of P_2S_5. The slurry was stirred to keep it from settling. Then about one-quarter of the volume of slurry was allowed to flow into the reaction flask. Upon heating this portion to 70°C., a self-sustaining reaction started, and the heat source was removed. The reaction mixture foamed strongly and copious amounts of vapor were given off. This vapor was condensed in the receiver, although some was lost due to insufficient condensing. After the initial reaction had subsided considerably, the remaining slurry was added in portions during one-half hour. The residue in the flask was a gummy solidified and carbonized foam. The distillate was reddish-yellow. The weight of distillate was 101.4 gm. equivalent to a yield of 29.7%. The liquid had a strong sulfide-type odor.

A second preparation was carried out, and 113.4 gm. of product were obtained, a yield of 39.5%. More efficient condensation was responsible for the increase in yield.

Steam distillation gave a light-yellow product. About 10%

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of the sample did not distill. Considerable H₂S was given off.

The attempt was made to prepare dithiotenyl phosphoryl chloride by heating 86.2 gm. (0.756 mole) of 5-methyl-2-hydroxythiophene with 58.0 gm. (0.378 mole) of $POCl_3$. At about 120°C. the reaction became uncontrolled, and the flask contents foamed up into the condenser. On cooling, the reaction mixture was a tar.

16. Diphenyl 1-Naphthyl Thiophosphate

a. Diphenyl Thiophosphoryl chloride.

In a 1-liter 2-neck round-bottom flask fitted with a thermo-well and an 80 cm. water-cooled reflux condenser were placed 339 gm. (2.0 moles) of thiophosphoryl chloride and 376 gm. (4.0 moles) of phenol. It was found necessary to add 2 wt. % of PCl_3 to catalyze the reaction, in accordance with the method of Gottleib (9). The reaction mixture was brought as rapidly as possible to 200°C. and held there for four hours. After removing the volatiles by preliminary distillations at atmospheric pressure and at aspirator vacuum, the residue was vacuum distilled. Only 33 gm. (0.116 mole) of diphenyl thiophoryl chloride, m.p. 65°C [literature value, 64°, (10)], was obtained. The major product, weighing 209 gm. was a yellow liquid b.p. 216°-217°/4 mm., with an odor of H₂S.

b. Diphenyl 1-naphthyl thiophosphate.

To a solution of 9.4 gm. (0.065 mole) of 1-naphthol dissolved in 250 cc. of pyridine was added 33 gm. (0.116 mole) of diphenyl thiophosphoryl chloride. Heat was liberated. After standing for about forty hours, the mixture was diluted with 500 cc. of CCl_4 and the solution washed four times with 250 cc. portions of water. After removing the volatile materials, a very small amount of a yellow, somewhat viscous liquid, b.p. 202°/0.17 mm., was obtained. Presumably, this was diphenyl 1-naphthyl thiophosphate, but there was not enough to work with.

17. Dibenzyl 1-Naphthyl Phosphate.

The unseccessful attempts to prepare this material are briefly described.

a. In a 1-liter, 3-neck, round-bottom flask equipped with a mechanical stirrer, reflux condenser and dropping funnel, and cooled in a water-bath, was placed 307 gm. (2.0 moles) of $POCl_3$. To this

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was added dropwise with stirring 432 gm. (4.0 moles) of benzyl alcohol. The addition was complete in two hours; stirring was continued for another two hours. After withdrawing the water-bath, considerable difficulty was experienced in keeping the reaction under control, even with gentle heating. Finally the reaction mixture was brought to 200°C, held there for three hours and allowed to cool. The product was a glass. Judging from a molecular weight determination, it was not a polymer.

b. A solution of 196 gm. (0.75 mole) of 1-naphthyl phosphoryl dichloride in one pound of pyridine was placed in a 1-liter, 3-neck flask equipped with a dropping funnel, thermowell and stirrer. The flask was placed in a water bath containing running tap water. To the pyridine solution, 162 gm. (1.5 moles) of benzyl alcohol was added dropwise at a rate such that the temperature of the reactants did not exceed 50°C. The addition was complete in three hours. After stirring for five hours, the reaction mixture was allowed to stand for fifteen hours. The mixture was diluted with five pounds CCl_4, then washed twice with one-liter portions of water, one liter of 3% HCl, and one liter of water. After drying and removal of the solvent, practically no residue remained.

c. In a 500 cc., 3-neck, round-bottom flask equipped with a dropping funnel, water-cooled condenser, thermometer and stirrer was placed 130.5 gm. (0.5 mole) of 1-naphthyl phosphoryl dichloride. The 1-naphthyl phosphoryl dichloride was heated to 100°C; then 108 gm (1.0 mole) of benzyl alcohol was added dropwise with stirring. The reaction was self-sustaining at 120°C. When addition was complete, the dark red reaction mixture was heated to 200°C. On cooling, the mixture became solid. Attempted vacuum distillation resulted in practically no distillate, the flask contents appearing to decompose.

d. A solution of 130.5 gm. (0.5 mole) of 1-naphthyl phosphoryl dichloride in one pound of pyridine was placed in a 3-neck, 1-liter flask equipped with a dropping funnel, stirrer and condenser. To this solution was added dropwise with stirring 108 gm. (1.0 mole) of benzyl alcohol. The flask was kept cool in a water bath, and the rate of addition of benzyl alcohol was such that the temperature remained around 40°C. After addition was complete, the solution was heated so as to reflux at 130°C. for two hours, then allowed to cool. The product was stored at ice-temperature to induce crystal formation.

A voluminous mass of crystals had formed. The supernatant liquid was decanted off and the crystal mass filtered. The crystal

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mass was then slurried in one pound of anhydrous ether, which was then drained off and added to the decanted mother liquor. A second pound of ether was added to this solution, causing considerable turbidity. The crystal mass appeared to be pyridine hydrochloride. The ether solution, after refrigeration, had deposited a viscous semi-solid. After decantation of the ether layer, the ether was distilled off. Again, practically no high-boiling residue was obtained. The viscous semi-solid appeared to be a syrup of pyridine hydrochloride.

18. Di-3-Pyridyl 1-Naphthyl Phosphate

The preparations listed below were carried out, but no product was obtained.

a. An abortive run using 4 moles of 3-pyridol and 2 moles of $POCl_3$ was stopped during the addition of the pyridol to the $POCl_3$. Considerable heat was liberated, and the pyridol apparently fused into a glass on the surface of the $POCl_3$. A sample of pyridol was fused to drive off any water which might be present, then ground up and added to $POCl_3$. The same type of reaction occurred.

b. A solution of 183 gm. (0.7 mole) of 1-naphthyl phosphoryl dichloride in approximately one-fourth pound of pyridine was placed in a 1-liter, 3-neck flask equipped with a dropping funnel, stirrer and thermowell. To this solution was added dropwise a solution of 133 gm. (1.4 moles) of 3-pyridol in three-fourths pound of pyridine. Very little heat of reaction was observed. After standing about sixty hours, the reaction product was diluted with five pounds of CCl_4, washed in the usual sequence with 1-liter portions of water, 5% KOH, water, 3% HCl and water. After drying and stripping off the solvent, an initial vacuum distillation gave 45 gm. of an orange-yellow viscous oil, b.p. 212°/0.15 mm. Attempted redistillation, however, yielded only 30 gm. of a yellow solid boiling at 105°-170°/0.17 mm. The product had apparently decomposed.

19. 5, 6, 7, 8-Tetrahydro-1-Naphthol

This preparation followed the method of Papa and Schwenk (11). A solution was made of 100 gm. of 1-naphthol in 3 liters of 10% NaOH solution. The solution was heated to 65°-75° C. and then 300 gm. of Raney Ni-Al alloy was added portion-wise over three and one-half hours. The solution was allowed to stand overnight. During the reaction, it was found desirable to add Dow-Corning Antifoam A to break

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the persistent foam which formed.

The solution was filtered from the nickel residue, then made strongly acid with conc. H_2SO_4. The reaction mixture was divided into two portions, and each portion was extracted three times with 200 cc. portions of ether. The ether solution was dried over anhydrous $MgSO_4$ and most of the ether distilled off. The residue was placed in an evaporating dish to allow the remaining ether to volatilize. The yield was about 30 gm. of crude product, melting at 72°C. Tetrahydronaphthol melts at 71°C. In all, five lots of product were made, a total of 125-150 gm. This material will be purified before being used as an intermediate.

IV. NOTEBOOK REFERENCES

The data from which this report was compiled is recorded in Southwest Research Institute Notebooks A 1011 and A 1025 and the card file prepared for Project No. 10-250-A.

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VI. LIST OF ABBREVIATIONS

AECD	Atomic Energy Commission Document (U. S.)
Beil.	Beilstein. Handbuch der Organischen Chemie
BIOS	British Intelligence Objective Subcommittee
CBCC	Chemical-Biological Coordination Center
CIOS	Combined Intelligence Objectives Subcommittee
FD	Foreign Document, Technical Information and Document Unit, Great Britain Board of Trade, London, England
FIAT	Field Intelligence Agency, Technical
MLO	Materials Laboratory Oil
OTS	Office of Technical Services, U. S. Department of Commerce
PB	Publication Board

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